TRANSPORT PHENOMENA IN MEMBRANES

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IN
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BY
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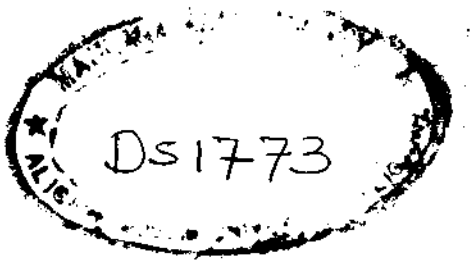
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CERTIFICATE

This is to certify that the dissertation entitled "Transport Phenomena in Membranes" submitted to the Aligarh Muslim University, Aligarh, describes the original work carried out by Mr. Dhananjay Prakash under my supervision and is suitable for the award of M.Phil degree in Chemistry.

(MOHAMMAD NASIM BEG)

A C K N O W L E D G E M E N T S

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Dhananjay Prakash

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C O N T E N T S

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INTRODUCTION

The steadily detoriating conditions of human life in civilized areas have much diminished the numbers of those who once considered the chief aim of science to be the unlimited subjugation and transformation of nature. The main importance of science, of course, never lay in this area and in the process of seeking a more thorough understanding of nature. Scientists have constantly imitated nature, especially, living nature. This direction appears even more promising at the present time: since the artificial tools, materials, or processes, developed are not only useful in themselves but, in addition provide models which on investigation provide a deeper understanding of the natural phenomena.

Membrane phenomena is a note-worthy product of this philosophy since the transport of materials across natural or artificial membranes has captured the interest of chemists, chemical engineers and biologists. Chemists and chemical engineers would like to understand the mechanism of transport so that with

the knowledge so gained they would be able to fabricate membranes of any desired property or properties to be used in fuel cells, nuclear technology, electrodialysis, ion selective electrodes, brakish water conversion and in many other processes. Biologists, however, would like to use artificial membranes as a simple model in order to understand the behaviour of complex biomembranes in terms of established physico--chemical principles. As a result, a huge valume of the literature related to transport phenomena across artificial membranes is available in various disciplines of science and technology: like analytical chemistry, physical chemistry, chemical physics, solid state physics, chemical engineerings, biophysics, biology, physiology and desalination.

It is too extensive to mention the whole literature describing membrane phenomena. The significant work in the field of electro-chemistry are by Helfferich (1), Merten (2),Marinsky (3),Spiegler (4,5), Hope (6),Plonsy (7), Lakshminarayanaiah (8,9), Cole (10),

Stein (11), Caplan and Mikulechy (12), Sandblam and Orme (13), Kotyk and Janacek (14), Harris (15), Schlogi (16), Bittar (17) and Keller (18). Numerous recent volumes describing the electrochemistry of membranes have been edited by Kotyk and Janacek (14), Eisenman (19) Danielli and Rosebberg (20), and Durst (21). In sensor techniques are now sufficiently advanced to have been discussed recently at several national and international conferences. This field has also been the subject of numerous general reviews (22-37), and as many specialized reviews: [Theory (38); industrial applications (39) air and water pollution (40-42), toxicology and hygiene (43); analysis of soil and water (44-47); plating and sugarbeet industry (48) and pharmaceuticals (49,50)]

W. Ostwald (51) in 1980 founded the electrochemistry of membranes by considering the properties of semipermeable membrane, that is, one which is impermeable to certain kinds of ions. The electric potential difference on such a membrane is a limiting case of the potential difference at liquid-liquid interface, when the

mobility of one kind of ion approaches zero. A small number of permeating ions penetrate through the interface and form an electrical double layer which is the source of electrical potential difference. The characteristics and existence of Donnan (52) membrane potential could be properly verified for porous membranes.

Theorell (53) Meyer and Sievers (54) have given the theory of membrane potential applicable to porous or compact oil types of membranes. In twenties and thirties, models for biological membranes were looked specially by Michaelis (55) and Sollner (56) Danielli and Davson (57) proposed a theory in which the membranes of cells were presumed to have the nature of very thin compact liquid membranes composed of bimolecular layers of phospholipids, covered on both the sides by a protein layer. Mueller and Co-workers (58) obtained for the first time very thin, artificial, biomolecular black, phospholipid membranes.

A membrane, in simple terms is defined as a phase usually heterogenous, acting as a barrier to the flow of molecular or ionic species present in the

liquid or vapour contacting the two surfaces. The term heterogeneous has been used to indicate the internal physical structure and the external physico-chemical performance (59-61). The notion of homogeneous vs heterogeneous membranes proves to be an important distinction from the point of view of mass transport. In dilute solution limit, the friction coefficient for mass transport by diffusion or migration are inconvertible by Onsager reciprocal relations and both can be related to jump distances and frequencies according to random walk models. As long as there are no prefferd regions of low friction in the membrane, it is isotropic on a molecular level and is consider to be homogeneous. Unformity of mesh on a molecular liquid is another view of homogeniety. Channel free solid and liquid membranes (Coherent gels and oil types) are usually homogeneous and low phase membranes (Solid crystallites inbedded in a non ionic resin) are heterogeneous.

Membranes are considered to be porous or nonporous depending upon the extent of solvent penetration (62). At the non porous extreme are membranes

which are non ionic and contain negligible transportable species at equilibrium. Ceramics, quartz, anthracene crystals and teflon films are the example of solid membranes. Organic liquid films like hydrocarbons and fluorocarbons in contact with aqueous electrolytes are the examples of liquid membranes. At the other extreme are the porous membranes, which can be solvated and will contain components from external phases. Among these are the non-ionic films such as cellophane, inorganic gels and loosely compressed powders in contact with aqueous solutions. These materials adsorb solvent from the surrounding media and may also extract other neutral molecules and ionic salts. More studied are the membranes of poly electrolytes, aqueous immiscible organic liquid electrolytes (1,8,29), various parchment supported inorganic precipitates (63-78), solid ion conducting electrolytes including silver halides, rare earth fluorides and alkali and aluminosilicate glasses (21,22,79,80). All these materials contain ionic or ionizable groups within the membranes which are capable of transport under diffusive or electric field forces. In addition,

these materials possess porosity. Polyelectrolytes tend to swell rapidly by solvent uptake. Liquid ion exchangers are very slow to take up water while inorganic salts have no tendency to hydrate. Glass membranes are complicated by simultaneous hydrolysis of the polyelectrolyte during uptake of water (81,82).

An important characteristic of electrolyte membranes is the presence of charged sites (83-88). If the ionic groups are fixed in a membrane as $-SO_3^-$ and $-COO^-$ attached to cation exchange resins, the membrane is considered to possess fixed sites. In glasses the fixed sites are $-SiO^-$ and AlO^- groups while in anion exchange resin membranes, these are NH_3^+, NH_2^+, $-N^+-$. The membranes having fixed ionogenic groups exclude co-ions by electrostatic repulsion. The extent of exclusion is governed by the concentration of the external electrolyte and the magnitude of the charge fixed to the membrane matrix. There will be a smaller number of coions than counterions by an amount equal to the number of fixed groups in ion-exchange membranes. The distinction between coions and counterions does not exist in non-ion exchange

membranes. The transport of non-electrolytes is governed by the relative sizes of permeating species and the membrane pores irrespective of the nature of the membrane. However, it is difficult to find a membrane either natural or artificial that would be free from carrying ionogenic groups either fixed to the three dimensional membrane metrix as seen in well characterized ion exchange membranes or adsorbed as found in colloidal systems (89).

The diffusion co-efficient in membrane phase depends on the size of the solvated ion. The observed sequence of mobility for alkalimetal ions, is in the order $Li^+ > Na^+ > K^+ > Rb^+ > Cs^+$(90-93). The retardation increases as the valency of the species is increased. This effect is more marked for counterions in cation exchangers than it is for counterions in anion exchangers. Retardation is stronger for counterions than for coions. This rises from the electrostatic attraction that counterions have for the oppositely charged fixed groups of the membrane. For coions there is no such attraction. Selective membranes

invariably contain more water than non-selective membranes. It is, therefore, to be expected on the basis of the presence of hydrated charged groups that the diffusion coefficients in selective membranes will be larger. These particular properties are of considerable industrial importance, as they determine the ultimate usefulness of the membrane in industrial dialysis or electrodialysis (94,95).

A membrane can be categorized according to whether it contains sites for ion exchange or it is site free and if it is an ion exchanger, according to whether its sites are free or mobile and whether the sites and their counterions are associated or dissociated. This type of classification has been presented by Eisemann, Sandblom and Walker (94). These authors have, however, restricted their discussion to membranes whose properties are considered to be homogeneous in the plane of the membrane and have avoided explicity with the complexities which result from either mosaic membranes, in which local eddy current (89) occur or series membranes in which space charge regions exist analogous to those at a p-n semiconductor junction(95).

Lakshminaryanaiah (8) has given a classification of artificial membranes of three basis of the reaction involved e.i. addition or condensation reaction.

Impedance measurements provide a powerful diagnostic tool for the analysis of many electro chemical systems (96-99). In order to understand the behaviour of complex living membranes, simple polymeric for some time (100), liquid bilayer membranes (101,102), parchment (103-106) and millipore (107-109) filter paper supported membranes in recent years have been used as models by a number of investigators. Warburg (110) developed the theory of diffusional impedances and derived the expression for it. The work of Macdonald (111) provides a systematic treatment of small signal a.c. responce of conducting cell and membranes. Archur and Armstrong (112) interpreted the complex impedance spectra for solid /electrolyte interfaces. S.H. White (96) studied the membrane capacitance under various conditions of surface charge and electrolyte concentration. Kobatake et al. (97) Studied the impedance of

surface membrane of protoplasmic drops. Membrane capacitance and resistance was found to be frequency dependent. Takashima et al (113) has shown that the parallel arrangement of resistance and capacitance may transformed to a series arrangement. A.E. Hill (114) while studying the ion transport through leaf gland cells of limonium measured the impedance characteristics of the whole leaf disc. The frequency characteristics was examined with a.c. bridge circuit. The a.c. responce to a rough elect - rode surface in contact with an aqueous electrolyte has been discussed by de Levie (115,116).

The technique of capacitance has been applied to many passive and excitable membranes (117-120). Early works of cole and curtis (119) and cole and Baker (121,122) demonstrate various unique features of nerve membranes. The analysis indicate that the effect of electrolyte concentration and bridge frequency on membrane capacitance is not due to electrode polarization but may be due to some structural changes in the membrane as discussed by chandler et al (123). The frequency dependence of the electrical impedance of a tissue is conveniently represented by the impedance locus, a graph of

reactive component against resistive component with frequency as implicit parameter. The impedance locus of a cell membrane is frequently a circular are with its center below the resistance axis (124).

A number of theoretical models [point charge model (125-130) and finite ion size model (115,116,131)] for the solid/electrolyte conductor interface have been used to interpret the impedance characteristics under various conditions of blocked, partially blocked and unblocked electrolyte depending upon the extent of penetration of the electrolyte to the electrode (115,116) Armstrong has attempted to use some of the theoretical models for aqueous electrolyte systems in order to obtain a simple model for the metal/superion conductor interphase which can explain some of the experimental observations that have been made on these systems (131).

In majority of cases, an electrochemical cell is better understood by a complicated network of resistance and capacitance. These show a complex behaviour

in the complex impedance plane. If an impedance spectrum is given, one can calculate the components of an equivalent circuit of resistance and capacitance responsible for it. Thus with the measurements on electro chemical cells, It is usual for investigator to measure the impedance of the cell and subsequently to find the probable equivalent circuit and the significance of different components. This is usually carried out by comparing the results with the theoretical model.

This dissertation describes the measurements of membrane impedance of parchment supported copper ortho arsenite membrane under various conditions of bathing electrolyte concentration and applied oscillator frequency in order to understand the mechanism of ionic transport through this membrane. The results are interpreted in terms of changes produced in the electrical double layer at the membrane/electrolyte interfaces. The values of membrane resistance/capacitance and impedance have been computed by considering different equivalent electrical circuit models.

E X P E R I M E N T A L

Parchment supported copper ortho Arsenite membrane has been prepared by the method of interaction as suggested by Beg and cowerkers (103-106). The Chemicals, copper sulfate and sodium ortho arsenite are of A.R. grade. Parchment paper was first dipped in deionized water for about two hours and then tied carefully to the mouth of a beaker containing 0.5 M copper sulfate solution. This was suspended in a solution of potassium hydroxide for 72 hours. The two solution (fresh solution) were interchanged and kept for another 72 hours. Precipitate of copper ortho arsenite diposits in the interstices of parchment paper. The membrane was than washed several times with deionized for the removal of free electrolyte. The membrane thus obtained were cut into a circular disc from the unit cross-sectional area and sealed between the two half cells of an electrochemical cell. The two half cells were filled with electrolyte solutions to equilibrate the membrane. The solutions were then replaced by purified mercury without removing the adhering surface liquids. Air bubbles, if any, on the membrane surface was removed by tilting the cells essembly. Mercury is likely to be oxidized to form mercuric oxide

which would form films on membrane faces and cause irreversibility. Use of purified mercury has eliminated this problem and has given reproducible results.

A universal LCR bridge 921 has been used to measure the electrical resistance and capacitance of the membranes. The membranes were equilibrated with lower concentration of sodium chloride initially then the higher concentration while measuring the resistance and capacitance of the membranes. The effect of oscillator frequency over the resistance and capacitance values have been observed for the membranes. A platinum wire coated with platinum black dipped in Hg was used as the electrode. The use of long electrode was preferred in order to avoid tip impedance(113).

RESULT AND DISCUSSION

The electrical resistance (R_x) and capacitance (C_x) across parchment supported copper ortho arsenite membrane equilibrated with different concentration of aquous sodium chloride solution over a frequency range of 1-6 KHz have been measured. These values are given in Tables I to IV.

The data refer to the fact that the R_x decreases with the increasing in electrolyte concentration and increasing in frequency. The decrease of R_x with increase of electrolyte concentration and magnitude of applied frequency are attributable, respectively to increased electrolyte uptake and fast exchange of polarity resulting the dielectric across the two surface of the membrane.

The magnitude of C_x increases with the increase in bathing electrolyte concentration. The increase in C_x may be ascribed to the changes produced in the dielectric properties (ϵ) and the effective thickness (d) of the membrane/electrolyte system in according with the equation for parallel plate capacitor.

TABLE -I :-

Electrical Resistance (R_x) and Capacitance (C_x) observed across Parchment supported Copper Ortho Arsenite Membrane Equilibrated with different concentration of Sodium Chloride at different Oscillator Frequencies (Temp = 30°C).

Oscillator frequency (Hz)	0.0001N NaCl		0.0005N NaCl		0.001N NaCl	
	R_x(Ω)	C_x(μf)	R_x(Ω)	C_x(μf)	R_x(Ω)	C_x(μf)
$1x10^3$	$1.10x10^3$	$8.80x10^{-3}$	$0.84x10^3$	$9.00x10^{-3}$	$0.620x10^3$	$12.00x10^{-3}$
$2x10^3$	$1.05x10^3$	$9.00x10^{-3}$	$0.83x10^3$	$9.50x10^{-3}$	$0.615x10^3$	$12.50x10^{-3}$
$3x10^3$	$1.00x10^3$	$9.20x10^{-3}$	$0.825x10^3$	$10.00x10^{-3}$	$0.610x10^3$	$13.00x10^{-3}$
$4x10^3$	$0.95x10^3$	$9.40x10^{-3}$	$0.815x10^3$	$10.50x10^{-3}$	$0.605x10^3$	$14.00x10^{-3}$
$5x10^3$	$0.90x10^3$	$9.60x10^{-3}$	$0.810x10^3$	$11.00x10^{-3}$	$0.600x10^3$	$14.50x10^{-3}$
$6x10^3$	$0.85x10^3$	$9.80x10^{-3}$	$0.800x10^3$	$11.50x10^{-3}$	$0.590x10^3$	$15.00x10^{-3}$

TABLE -II :-

Electrical Resistance (R_x) and Capacitance (C_x) observed across Parchment supported copper Ortho Arsenite Membrane Equilibrated with different concentration of Sodium Chloride at different Oscillator Frequencies (Temp=30°C).

Oscillator frequency(Hz)	0.005N NaCl		0.01N NaCl		0.05N NaCl	
	R_x(Ω)	C_x(μf)	R_x(Ω)	C_x(μf)	R_x(Ω)	C_x(μf)
$1x10^3$	$2.10x10^2$	$4.50x10^{-2}$	$1.45x10^2$	$6.80x10^{-2}$	$0.44x10^2$	$21.50x10^{-2}$
$2x10^3$	$2.05x10^2$	$4.60x10^{-2}$	$1.40x10^2$	$6.90x10^{-2}$	$0.43x10^2$	$22.50x10^{-2}$
$3x10^3$	$2.00x10^2$	$4.70x10^{-2}$	$1.35x10^2$	$7.00x10^{-2}$	$0.42x10^2$	$23.00x10^{-2}$
$4x10^3$	$1.95x10^2$	$4.80x10^{-2}$	$1.30x10^2$	$7.10x10^{-2}$	$0.41x10^2$	$24.00x10^{-2}$
$5x10^3$	$1.90x10^2$	$4.90x10^{-2}$	$1.25x10^2$	$7.20x10^{-2}$	$0.40x10^2$	$25.00x10^{-2}$
$6x10^3$	$1.85x10^2$	$5.00x10^{-2}$	$1.20x10^2$	$7.30x10^{-2}$	$0.39x10^2$	$26.00x10^{-2}$

TABLE -III :-

Electrical Resistance (R_x) and Capacitance (C_x) observed across Parchment supported Copper Ortho Arsenite Membrane Equilibrated with different concentration of Sodium Chloride at different Oscillator Frequencies (Temp= 30°C).

Oscillator frequency(Hz)	0.1N NaCl		0.5N NaCl		1.0N NaCl	
	R_x(Ω)	C_x(μf)	R_x(Ω)	C_x(μf)	R_x(Ω)	C_x(μf)
$1x10^3$	2.4x10	$3.90x10^{-1}$	0.70x10	$1.40x10^0$	0.39x10	$2.80x10^0$
$2x10^3$	2.35x10	$3.95x10^{-1}$	0.60x10	$1.50x10^0$	0.38x10	$3.00x10^0$
$3x10^3$	2.30x10	$4.00x10^{-1}$	0.55x10	$1.60x10^0$	0.37x10	$3.10x10^0$
$4x10^3$	2.25x10	$4.10x10^{-1}$	0.50x10	$1.65x10^0$	0.35x10	$3.20x10^0$
$5x10^3$	2.20x10	$4.20x10^{-1}$	0.45x10	$1.70x10^0$	0.35x10	$3.30x10^0$
$6x10^3$	2.15x10	$4.30x10^{-1}$	0.40x10	$1.75x10^0$	0.32x10	$3.40x10^0$

TABLE -IV : Electrical Resistance (R_x) and capacitance (C_x) observed across Parchment supported copper Ortho Arsenite Membrane Equilibrated with different concentration of Sodium Chloride at 1KHz (Temp = 30°C)

Electrolyte conc. (M/L)	R_x (Ω)	C_x (μf)
$1x10^{-4}$	1100.0	0.0088
$5x10^{-4}$	840.0	0.0090
$1x10^{-3}$	620.0	0.0120
$5x10^{-3}$	210.0	0.0450
$1x10^{-2}$	145.0	0.0680
$5x10^{-2}$	44.0	0.2150
$1x10^{-1}$	24.0	0.3900
$5x10^{-1}$	7.0	1.4000
$1x10^{0}$	3.9	2.8000

$$C_x = \epsilon / 36\pi \times 10^{11} d \qquad -(1)$$

The increase in C_x may be referred to the increase in electrolyte concentration and decrease in the value of d probably due to the deswelling of membrane because of squeezing of water molecules from the membrane framework by the incoming ions (132,133).

In order to have a better understanding to the mechanism of flow of ions through the membrane, of electrochemical properties and the electrical circuit associated with the system under investigation, impedance, membrane resistance and membrane capacitance have been evaluated on the basis of an equivalent electrical circuit model (Figure 1). For this circuit, Lakshminarayanaiah and Shane (134,135) have proposed the following relationships.

$$X_x = 1/\omega C_x \qquad -(2)$$

$$R_m = R_x \left[1 + \left(\frac{X_x}{R_x}\right)^2 \right] \qquad -(3)$$

$$C_m = (X_x/R_x)\ (1/\omega R_m) \qquad -(4)$$

and

$$Z = (R_x^2 + X_x^2)^{1/2} \qquad -(5)$$

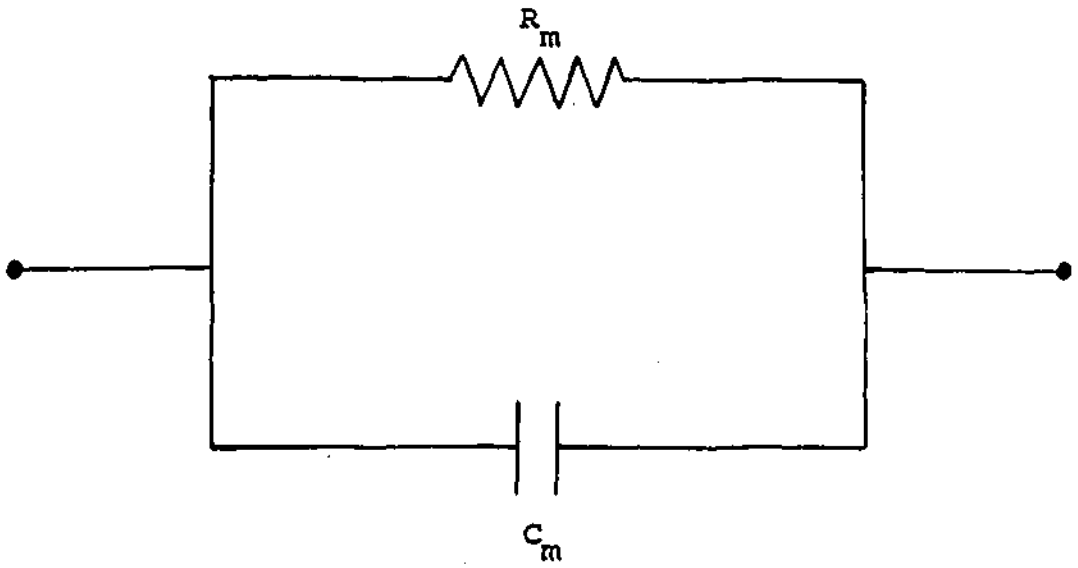

Fig. 1. The equivalent electrical circuit for a simple membrane. R_m and C_m are membrane resistance and membrane capacitance respectively.

Where X_x is the reactance, R_x and C_x are the electrical resistance and electrical capacitance observed for the model membrane equilibrated with different concentration of the univalent electrolytes, R_m and C_m are the membrane resistance and capacitance, Z is the impedance and $\omega = 2\pi f$, f is the applied frequency used to measure R_x and C_x.

The values of R_m, C_m and Z evaluated with the aid of equation 3,4 and 5 have been summarised as a function of bathing electrolyte concentration and applied oscillator frequency for the copper ortho arsenite membrane, are given in Tables V to VIII.

As is clear from table V, the decrease in R_m with increase in bathing electrolyte concentration may be ascribed due to progressive accumulation of ionic species with in the membrane, thus making the membrane more and more conducting, while the decrease in R_m with increase of applied frequency may be due to the fast exchange of polarity resulting in a leakage of charge through the dielectric across the two surface of the membrane (Table VI).

The decrease of R_m with increase of electrostatic field strength of the permeant can be discussed by considering the effect of permeants on the structure of water. Water is open structured and full of the cavities similar to those of ice. These cavities are believed to contain a dense liquid composed of non hydrogen bonded molecules. Clustered and nonhydrogen bonded water molecules are in equilibrium with one another. The sensitive order disorder equilibrium is responsible for its unusual properties as its ability to increase or decrease in order by interaction with cations. The cations with high electrostatic field strength, e.g., Na^+, increase the structuredness of water while those with low electrostatic field strength, e.g. K^+, NH_4^+ decrease it. The cation of former catagory increase the viscosity and permeate less readily than the cation of the latter catagory, which decrease the viscosity (136).

The C_m increase with an increase of bathing electrolyte concentration, such a membrane behaviour can be attributed to the changes produced in the dielectric properties and effective thickness of the membrane. The surface charges between the membrane and electrolyte

TABLE -V :- Calculated values of Membrane Resistance (R_m) Membrane Capacitance (C_m) and Impedance (Z) from eq.(3), (4) and (5) for Parchment supported Copper Ortho Arsenite Membrane Equilibrated with different concentrations of Sodium Chloride at 1 KHz (Temp = $30^{\circ}C$).

Electrolyte Conc. (M/L)	$R_m(\Omega)$	$C_m(\mu f)$	$Z(\Omega)$
$1x10^{-4}$	$2985.90x10^{2}$	$8.77x10^{-3}$	$181.23x10^{2}$
$5x10^{-4}$	$3734.67x10^{2}$	$8.98x10^{-3}$	$177.71x10^{2}$
$1x10^{-3}$	$2845.97x10^{2}$	$11.97x10^{-3}$	$132.83x10^{2}$
$5x10^{-3}$	$598.16x10^{2}$	$44.84x10^{-3}$	$35.44x10^{2}$
$1x10^{-2}$	$379.40x10^{2}$	$67.76x10^{-3}$	$23.45x10^{2}$
$5x10^{-2}$	$125.09x10^{2}$	$214.25x10^{-3}$	$7.41x10^{2}$
$1x10^{-1}$	$69.66x10^{2}$	$388.74x10^{-3}$	$4.08x10^{2}$
$5x10^{-1}$	$18.53x10^{2}$	$1395.20x10^{-3}$	$1.13x10^{2}$
$1x10^{0}$	$8.311x10^{2}$	$2790.29x10^{-3}$	$0.56x10^{2}$

TABLE -VI: Calculated values of Membrane Resistance (R_m), Membrane Capacitance (C_m) and Impedance(Z) from eqs.(3),(4) and (5) for Parchment Supported Copper Ortho Arsenite Membrane Equilibrated with 1.0N Sodium Chloride solution at different Oscillator Frequencies (Temp = 30°).

Oscillator frequency	R_m(Ω)	C_m(μf)	Z(Ω)
$1x10^3$	831.14	2.790	56.93
$2x10^3$	188.60	2.942	26.77
$3x10^3$	82.91	2.962	17.51
$4x10^3$	47.71	2.965	12.92
$5x10^3$	31.14	2.989	10.21
$6x10^3$	9.00	3.969	5.36

TABLE -VII :- Calculated Magnitudes of Membrane Resistance (R_m) and Membrane Capacitance (C_m) for Parchment supported Copper Ortho Arsenite Membrane Equilibrated with Different Electrolyte Concentrations at 1 KHz (Temp = 30^0) .

Conc. (M/L)	R_m (Ω)			C_m (μf)			Z (Ω)		
	NaCl	KCl	NH_4Cl	NaCl	KCl	NH_4Cl	NaCl	KCl	NH_4Cl
$1x10^{-4}$	$2985.90x10^2$	$3464.20x10^2$	$16315.43x10^2$	$8.77x10^{-3}$	$6.97x10^{-3}$	$2.89x10^{-3}$	$181.23x10^2$	$227.96x10^2$	$54.39x10^2$
$1x10^{-3}$	$2845.97x10^2$	$5309.96x10^2$	$26091.11x10^2$	$11.97x10^{-3}$	$8.99x10^{-3}$	$3.59x10^{-3}$	$132.83x10^2$	$177.01x10^2$	$442.38x10^2$
$1x10^{-2}$	$379.40x10^2$	$388.48x10^2$	$285.28x10^2$	$67.76x10^{-3}$	$63.73x10^{-3}$	$49.41x10^{-3}$	$23.45x10^2$	$24.93x10^2$	$31.84x10^2$
$1x10^{-1}$	$69.66x10^2$	$713.55x10^2$	$517.94x10^2$	$388.74x10^{-3}$	$130.07x10^{-3}$	$75.78x10^{-3}$	$4.08x10^2$	$12.24x10^2$	$20.95x10^2$
$1x10^0$	$8.31x10^2$	$61.84x10^2$	$74.53x10^2$	$2790.29x10^{-3}$	$999.83x10^{-3}$	$894.24x10^{-3}$	$0.56x10^2$	$1.76x10^2$	$1.76x10^2$

TABLE -VIII: Calculated Magnitude of Membrane Resistance(R_m) and Membrane Capacitance (C_m) for Parchment supported Copper Ortho Arsenite Membrane Equilibrated with 0.01 M solutions of Different Electrolytes at different Oscillator Frequencies. (Temp= 30°C).

Oscillator Frequency (Hz)	R_m (Ω) NaCl	KCl	NH_4Cl	C_m (μf) NaCl	KCl	NH_4Cl	Z(Ω) NaCl	KCl	NH_4Cl
$1x10^3$	$379.40x10^2$	$388.48x10^2$	$285.31x10^2$	$67.76x10^{-3}$	$63.73x10^{-3}$	$49.37x10^{-3}$	$23.45 x10^2$	$24.88x10^2$	$31.84 x10^2$
$2x10^3$	$96.48x10^2$	$101.50x10^2$	$72.36x10^2$	$68.00x10^{-3}$	$64.04x10^{-3}$	$49.54x10^{-3}$	$11.53x 10^2$	$12.24x10^2$	$15.31x10^2$
$3x10^3$	$43,93x10^2$	$45.84x10^2$	$31.51x10^2$	$67.85x10^{-3}$	$64.22x10^{-3}$	$49.25x10^{-3}$	$7.58x 10^2$	$8.04x10^2$	$9.65x10^2$
$4x10^3$	$25.47x10^2$	$26.60x10^2$	$17.91x10^2$	$67.38x10^{-3}$	$63.50x10^{-3}$	$47.67x10^{-3}$	$5.60x10^2$	$5.94x10^2$	$6.85x10^2$
$5x10^3$	$16.90x10^2$	$18.16x10^2$	$12.08x10^2$	$66.67x10^{-3}$	$63.17x10^{-3}$	$44.41x10^{-3}$	$4.42x10^2$	$4.68x10^2$	$5.30x10^2$
$6x10^3$	$12.21x10^2$	$13.08x10^2$	$8.81x10^2$	$65.83x10^{-3}$	$62.42x10^{-3}$	$40.88x10^{-3}$	$3.63x10^2$	$3.84x10^2$	$4.21x10^2$

solution may be responsible for the increase of membrane capacitance with the increase in the magnitude of applied frequency.

The electrical double layer theory (99) may also be used to interpret the change produced in the magnitude of C_m with the change in bathing electrolyte concentration. The electrical double layer at the membrane / solution interface has been utilized in several studies to account for various membrane behaviour (99,137). The polarization charge on the geomatric capacitor in the form of diffused double layer plays an important role and affects the overall membrane capacitance(138,139). The applied frequency across the membrane has been found to affect the double layer capacitance by the movement of ions across it. In order to investigate the impedance characteristics of the membrane/electrolyte system and the double layer effect, the equivalent electrical circuit has been analyzed further and may be represented as in Figure 2. This circuit, according to Armstrong (140) represents a solid smooth surface in contact with the penetrating electrolyte and refers to ideal impedance spectra on

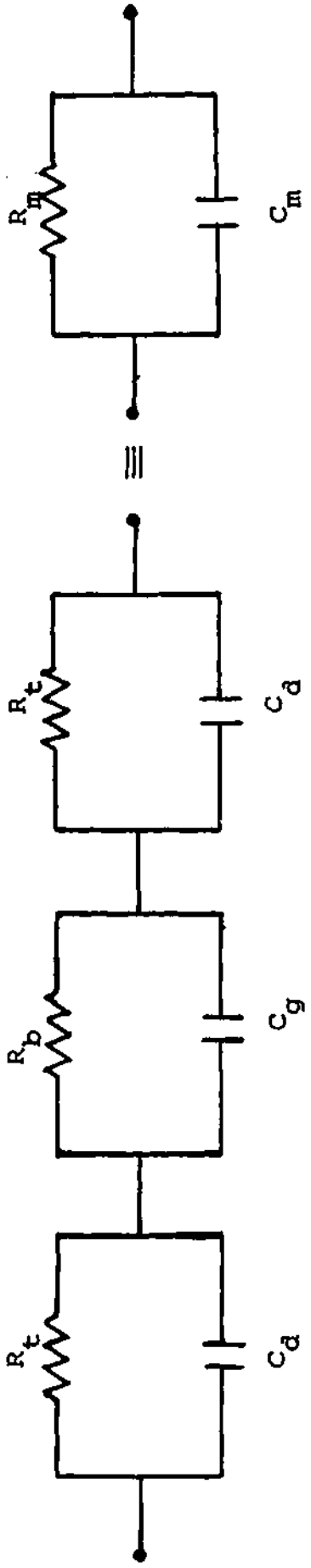

Fig. 2. Equivalent electrical circuit for a membrane / electrolyte system.

complex plane as shown by the dotted lines in Figure 3(a-e). Where C_g is the specific geomatric capacitance which is assumed to depend upon the structural details of the polymer network of which the membranes are composed, C_d is the interfacial electrical double layer capacitance, R_b is the bulk resistance of the membrane, and R_t is the charge transfer resistance between membrane/electrolyte interface assuming the ion transfer process to be single step.

The impedance of the proposed equivalent electrical circuit (Figure 2) for the membrane/electrolyte system is given by

$$\frac{2R_t}{1+j\omega C_d R_t} + \frac{R_b}{1+j\omega C_g R_b} = \frac{R_m}{1+j\omega C_m R_m} \quad \text{----------(6)}$$

The real and imaginary parts of eq (6) are given by

$$\frac{R_m}{1+\omega^2 C_m{}^2 R_m{}^2} = \frac{2R_t}{1+\omega^2 C_d{}^2 R_t{}^2} + \frac{R_b}{1+\omega^2 C_g^2 R_b{}^2} \quad \text{------(7)}$$

$$\frac{C_m R_m{}^2}{1+\omega^2 C_m{}^2 R_m^2} = \frac{2C_d R_t{}^2}{1+\omega^2 C_d{}^2 R_t{}^2} + \frac{C_g R_b{}^2}{1+\omega^2 C_g{}^2 R_b^2} \quad \text{-------(8)}$$

Equation (8) can be approximated at higher oscillator frequencies as

$$\frac{1}{C_m} = \frac{1}{C_g} + \frac{2}{C_d} \qquad \text{--------} \quad (9)$$

Which indicate that the membrane/electrolyte system may be considered to be composed of three capacitors arranged in series. The geomatric capacitor is placed between the two interfacial double layer capacitors as suggested by Armstrong(112). For high electrolyte concentrations or significant surface charge (99,141), $1/C_g \gg 2/C_d$ so that $C_m \approx C_g$.

Now taking this value of C_m as C_g (at 1N NaCl solution), the different values of C_d at other electrolyte concentrations are calculated using eq(9). It is found that the value of C_d increases with increase in electrolyte concentration. C_m should differ considerably from C_g when $1/C_g \approx 2/C_d$. This situation prevails in the absence of surface charge at low electrolyte concentrations.

The exact form of the double layer capacitance depends upon the fixed surface charge (σ_s) and the membrane potential (V_m). If $\sigma_s = 0$, then (141)

$$C_d = \frac{\epsilon_o \epsilon_w \ \text{Sin h}\alpha}{(1/k)\alpha} \qquad \text{----(10)}$$

Where $\epsilon_o = 8.85 \times 10^{-14}$ F/Cm, ϵ_w is the dielectric coefficient of water, α is a constant which takes into account the structural details of membrane polymer, and (1/k) is the Debye-Huckle length given by

$$1/k = \left(\frac{4.31 \times 10^{-8}}{(2x\mu)1/2} \right) \qquad \text{-----(11)}$$

Where μ is the ionic strength of bathing electrolyte solution, α is determined from the transcendental equation

$$\left[\frac{\epsilon_o \epsilon_w}{(1/k)\ C_g} \cdot \text{Sin h}\alpha + 2 \right] = \frac{V_m}{2(RT/F)} \qquad \text{-------(12)}$$

or alternatively from

$$C_m V_m = \sigma P = 4\ FC\ (1/k)\ \text{Sin h}\alpha \qquad \text{------(13)}$$

Where σ_p is the polarization charge on the capacitor. Equation (10) can be reduced to

$$C_d = \frac{\epsilon_o \cdot \epsilon_w}{(1/k)} \qquad \text{------(14)}$$

If $V_m \ll RT/F$ so that Sin h$\alpha = \alpha$. The value of C_d calculated from eq (14) at different electrolyte concentrations are given in Table IX. The difference in the values of C_d Calculated from eqs (9) and (14) is attributed to the presence of polarizing charge and other structural details of membrane matrix.

The frequency dependence of the electrical impedance of membrane is conveniently represented by the complex impedance spectra (112). The impedance spectra of complex plane for the different concentrations of copper ortho arsenite membrane is represented in figure 3 (a-e). The dotted scrambling according to Armstrong represents a solid smooth surface in contact with the penetrating electrolyte and refers to the ideal impedance spectra. The experimental data follow the theoretical predictions at higher frequencies where as at a lower frequency region, there is a marked deviation from ideal behavior may be due to nonhomogeneity and rough membrane surface (142-144).

It may, therefore, be concluded that the membrane/electrolyte system can be represented by a model equivalent electrical circuit as shown in figure 2

TAHLE -IX : Calculated values of Interfacial Double layer capacitance (C_d) for Parchment supported Copper Ortho Arsenite Membrane Equilibrated with different concentrations of Sodium Chloride at 1KHz (Temp = $30^{o}C$).

Electrolyte conc. (M/L)	C_d from eq. (14) (μf)	C_d from eq. (9) (μf)
$1x10^{-4}$	2.279	$1.759\ x10^{-2}$
$5x10^{-4}$	5.097	$1.796x10^{-2}$
$1x10^{-3}$	7.208	$2.405x10^{-2}$
$5x10^{-3}$	16.118	$9.116x10^{-2}$
$1x10^{-2}$	22.795	$13.889x10^{-2}$
$5x10^{-2}$	50.974	$46.419x10^{-2}$
$1x10^{-1}$	72.141	$90.335x10^{-2}$
$5x10^{-1}$	161.189	$558.113x10^{-2}$
$1x10^{o}$	227.958	-

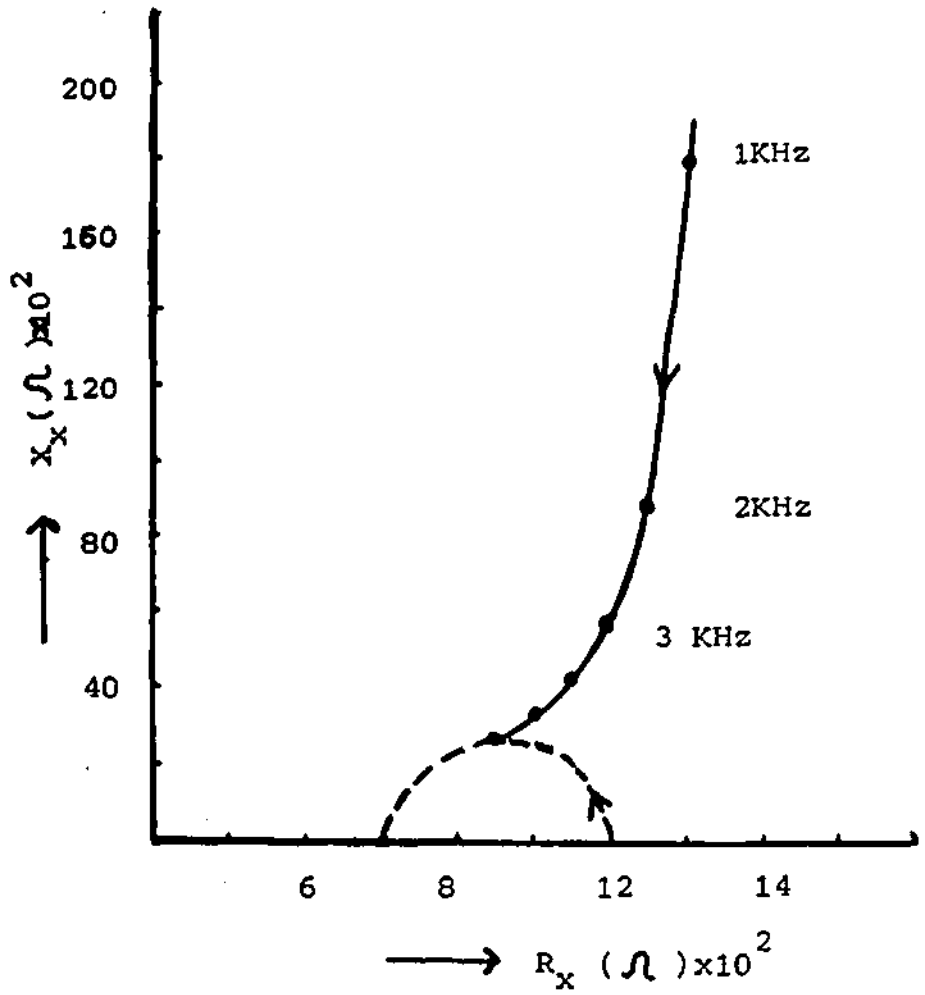

Fig.3(a) Theoretical (---) and experimental complex Impedance Spectra for Copper Ortho Arsenite membrane equilibrated with 0.0001 N solution of NaCl.

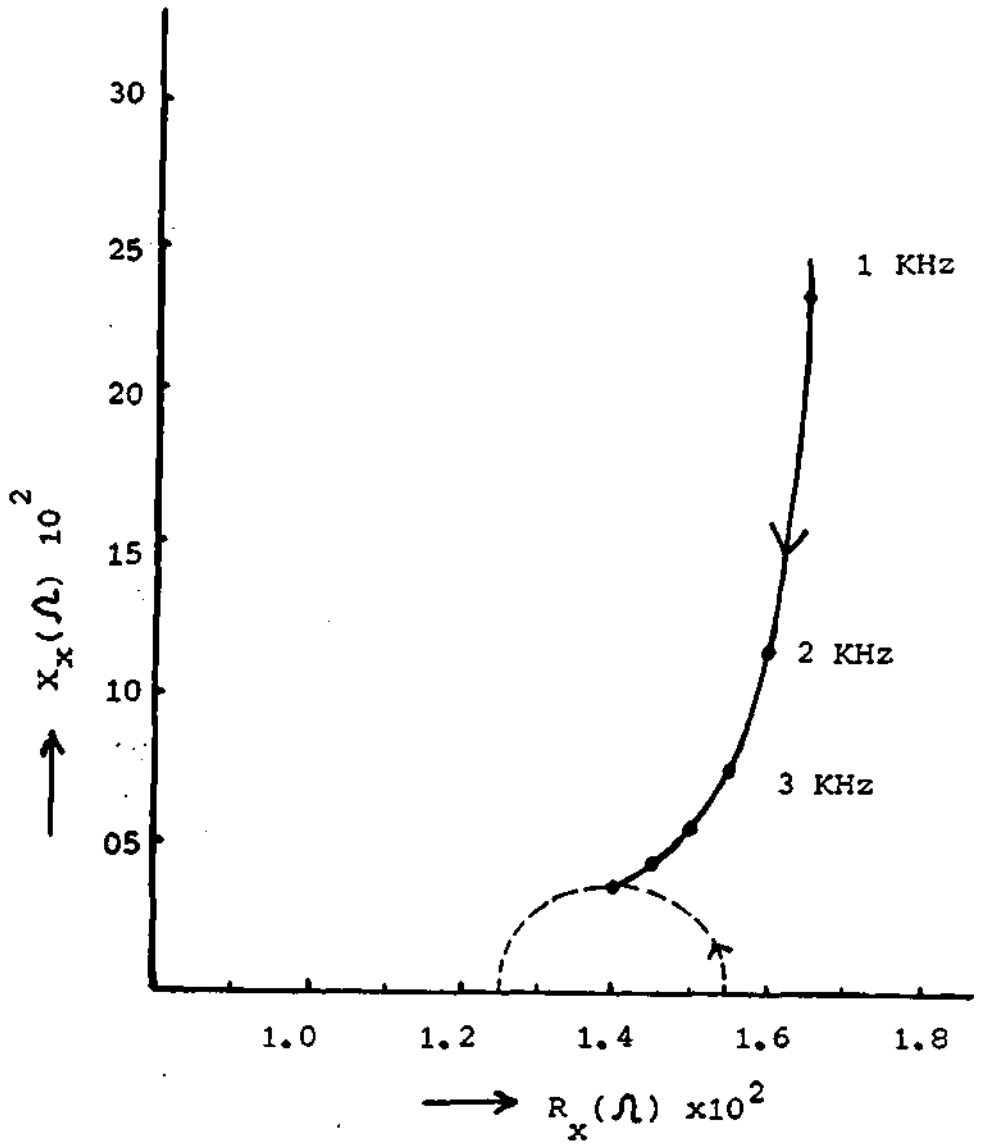

Fig. 3(b) Theoretical (---) and experimental (-) complex Impedance Spectra for Copper Ortho Arsenite membrane equilibrated with 0.01 N solution of NaCl.

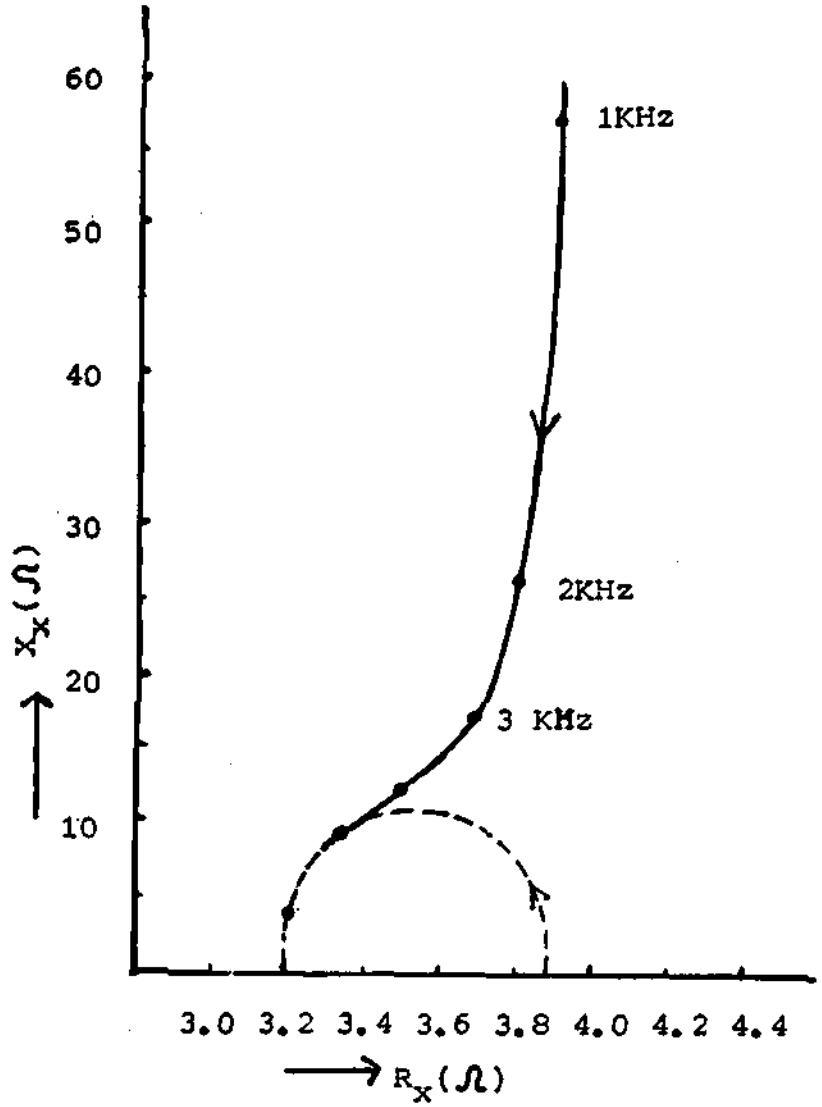

Fig.3(c). Theoretical (--) and experimental(-) complex Impedance Spectra for Copper Ortho Arsenite membrane with equilibrated with 1.0 N solution of NaCl .

and the values of membrane capacitance (C_m) as a function of electroyte concentration is accurately predicted by double layer theory. This type of behavior is in aggrement with our earlier findings of membrane potential measurements with copper ortho arsenite membrane (145) as well as in agreement with Tien and Ting (146) for bilayer membranes that the electrical double layer at the interfaces control the diffusion process, at least in dilute concentration ranges (147).

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A B S T R A C T

Transport phenomena in membranes have acquired considerable significance during the last few decades because of its direct impact in desalination, ion sensor techniques, fuel cell technology, electrical storage batteries, biology, medicine and several other processes. The investigators from various disciplines e.g. , chemist, chemical engineers, physicists and biologists have contributed extensively, although the aims and the starting points have been quite different. The literature in this field is enormous but not very coherent.

The present quarter of this century has witnessed a rapid growth in the development and use of model membranes for carrying out investigations of various aspects of bio-electric phenomena. A number of investigators have developed simple, well defined and stable model membranes. Based on the structure and composition of biomembranes, lipid bilayer membranes have been considered as the most realistic model except for few shortcomings. Parchment paper, which mimic some of the

functional properties of electrolyte cell and gastric mucosal membranes, have been used to study the rectification phenomena in biological systems and in some other physico-chemical studies. Inorganic precipitate membranes, owing to their stability at higher temperatures, ion exchange power and strong adsorption characteristics have been used in many processes of nuclear and chemical technology and electrosynthesis of organic compounds in some non conducting media.

This dissertation describes the measurement of electrical resistance R_x and capacitance C_x of parchment supported copper ortho arsenite membrane equilibrated with different concentrations of sodium chloride and at various frequencies. The data refer that R_x decreases while C_x increases with the increase in bathing electrolyte concentration. The decrease in R_x with the increase in electrolyte concentration may be ascribed due to progressive accumulation of ionic species within the membrane and thus making the membrane more and more conducting. The increase in C_x may be

attributed due to the changes produced in the dielectric properties and effective thickness of the membrane.

A membrane-electrolyte system is usually represented by an equivalent electrical circuit. Considering structural details of membrane matrix and interfacial electrical double layers at the membrane-solution interfaces, the circuit has been analysed in terms three units of resistance and capacitance, one of which represents membrane matrix and the other two for interfacial electrical double layers. At higher frequencies, the equation for a membrane-electrolyte system takes the following limiting from, viz.,

$$\frac{1}{C_m} = \frac{1}{C_g} + \frac{2}{C_d}$$

This equation suggests that the membrane capacitance is the resultant of three capacitors placed in series. The specific geomatric capacitor is placed between the two interfacial double layer capacitors.

for high electrolyte concentrations and/or significant surface charge,

$\frac{1}{C_g} \gg \frac{2}{C_d}$ So that $C_m \backsim C_g$. Now taking this value of can as C_g, different values of C_d at lower electrolyte concentrations were calculated using above equation. It has been found that value of C_d increases with the increase in electrolyte concentrations probably due to decrease in the thickness of interfacial double layer (debye length) and /or accumulation of ions at the membrane-solution interfaces.

The frequency dependence of the electrical impedance of membranes has been represented by the complex impedance spectra in the form of a semi circle. The semicircle represents a solid smooth surface in contact with the penetrating electrolyte and refers the ideal impedance spectra. The experimental data follow the theoretical predictions at higher frequencies while at lower frequencies, there is a mark deviation from ideal behavior may be due to roughness and non-homogenity of the membrane.